1 Introduction

1.1 Motivation

In the year 1795, in response to the food scarcity and logistic challenges of his army, Napoleon Bonaparte offered a reward of 12000 francs for an appropriate method to preserve food [1]. In 1810 a French confectioner called Nicolas Appert responded with a method to store sterilized food and seal the container, in his case glass jars. In the same year, the British merchant Peter Durand was granted a patent by King George III for the same preservation method, though he used tin-plated steel cans.

Today, one on the most widespread forms of food packaging still is the metal can. Health and safety of the foodstuffs stored in the cans have been the topic of investigation ever since their inception, and in certain regions of the world, aluminum is used instead. However the most successful form has long been tin-plated steel leading to the widespread use of the phrase *tin can*. In fact, the market has expanded to modern consumables such as paints, chemicals and aerosols. Today's cans are produced *en masse*, with millions of tons of tin-plated steel per year.

The material examined in this thesis is an alternative to the aforementioned tin-plated steel can. It is a laminate of *electrolytically chrome coated steel* (ECCS) with *polyethylene terephthalate* (PET) polymer layers on both sides. The basic advantages of this materials system are twofold:

- No tin is required. This should reduce costs significantly and improve recyclability.
- No lubricants are required during the processing steps. The PET layers serve as a soft layer between the steel and the forming tools.

The economics of such an alternative process (less and cheaper materials; fewer production steps; less waste) are very attractive, so there is good reason to develop it for the food industry. This involves ensuring that the functions of the tin-plated steel can are available to the polymer-laminated steel can. Such functions include resistance to corrosion but also control of the appearance – much of the commercial success of packaging is attributed to attractive images and paints applied to the cover.

An improved understanding of the materials system, especially the behavior of the materials at the metal/polymer interface, is expected to give us more control over the corrosion resistance and appearance. However the study of such an interface is a major challenge due to the differences between the materials – and few materials are as different as PET and steel. As a consequence fundamental research is needed to make a step forward.

In a serious attempt to study this material system some generic progress must be made: the knowledge obtained about the PET/ECCS interface from this research is not only useful for a specific application – it may be used to understand composite materials better.

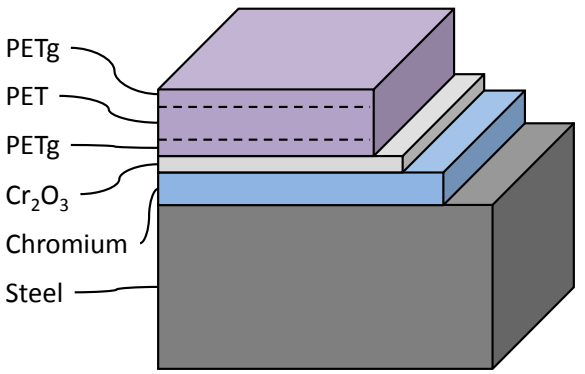

Figure 1.1: Schematic view of the structure of PET/ECCS laminate material (not to scale). The steel sheet is 225 µm thick, and is laminated on both sides with 6-15 nm chromium, on which a 0.6-2.5 nm chromium oxide layer is found. The ECCS is covered with a 10-30 µm multilayer PET system.

1.2 State of the art

The materials system to be studied and understood poses multidisciplinary questions. Understanding is required of metal plasticity, polymer deformation, interface chemistry and cracking behavior. Phenomena unique to each of these

fields are present at the interface, which makes it particularly difficult to unravel. A few relevant issues are discussed below.

1.2.1 Cracking behavior

The corrosion experiments in [2] show the formation of white and brown blisters and delamination fronts in addition to corrosion. This is the result of the loss of adhesion at the interface, i.e. a crack between the metal and polymer. Fedorov et al. [3]–[5] were able to induce similar blisters in a controlled fashion using a laser setup. This allowed them to study the adhesive energy and the traction at the interface. The time scale of these experiments was sufficiently short so that the response of the polymer could be well approximated by its (an)elastic behavior.

Van den Bosch et al. have studied the cracking behavior extensively using peel tests [6]–[11] and developed a "cohesive zone" formulation to describe loss of adhesion – taking into account the fibrils observed at the peeling interface during such tests. The challenge of such tests is that in determining forces of peeling there is substantial plastic deformation of the PET. Since PET is a very ductile material, a large amount of energy exerted during the tests is dissipated as work. This makes it difficult to distinguish the properties of the interface itself.

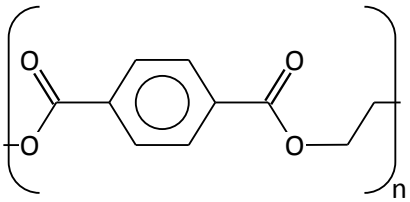

Figure 1.2: Molecular structure of PET. The polymer chains average around 27 kg/mol, meaning that the number of repeats n *is around 140.*

1.2.2 Interface chemistry

Adhesion of the polymer to the metal is generally believed to be based on hydrogen bond interactions. The ECCS is essentially ferritic steel covered with a 15 nm chromium layer, which itself is covered by a thin chromium oxide (Cr_2O_3) passivation layer, see Figure 1.1. This passivation layer is hydrogenated, resulting in –OH groups at the surface, which are expected to interact in the conventional manner with the ester and carboxylic acid groups in PET. In a very wet environment, water may also form hydrogen bonds with the surface [12], [13]; in theory this bonding is stronger than that of the ester groups, but not as strong as

the bonding between the carboxylic acid end groups and the surface (see Figure 1.3).

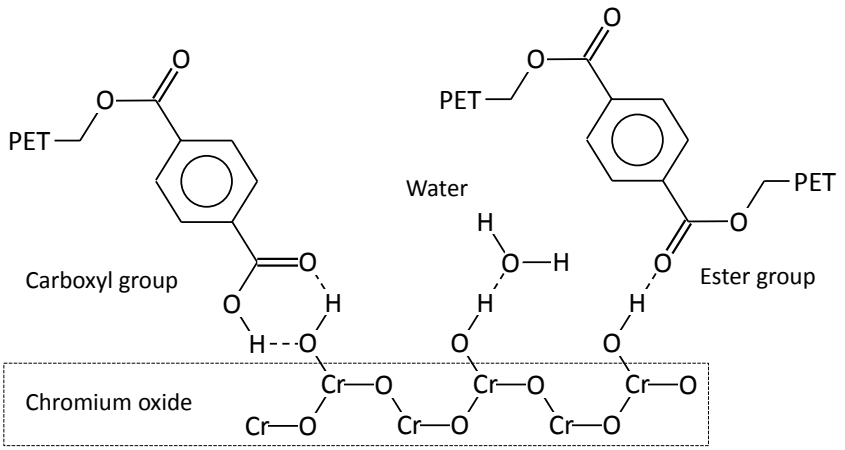

Figure 1.3: Functional groups expected to compete for hydrogen bonds with the hydroxide surface groups, ordered from strong (left) to weaker (right).

Loss of adhesion, even on a microscopic scale, may result in the formation of a liquid phase at the interface. Water and oxygen can dissolve in the solid PET and reach the interface by diffusion. Certain components such as acetic acid do not dissolve in PET significantly, but may undergo a reversible reaction forming a component which does (e.g. acetic acid anhydride). Once the right mixture of chemicals is present at the interface, corrosion can occur [14]. Boelen et al. [14] identify several more factors in the process, such as deformation. It is suggested that high strain results in the exposure of iron – which is much more susceptible to corrosion than an uninterrupted chromium oxide layer.

1.2.3 Polymer deformation

Polyethylene terephthalate (or PET, see Figure 1.2) is a complex material system, as has been explored by e.g. Rastogi [15], [16]. PET crystallizes slowly and is semi-crystalline, meaning the crystalline conformation and amorphous conformation co-exist. The mechanical properties of PET depend sensitively on the complete thermal history of the sample after synthesis or melting. Rastogi recorded the presence of shear bands and cracks, not only as a result of the thermal history of PET but also correlating with the roughness of the underlying substrate – such as protruding grains and glide steps in the metal grains.

The PET used in the currently studied material is a multilayer system in itself: it consists of a layer of semi-crystalline PET sandwiched between two layers of PET

functionalized with glycol groups. These reduce the crystallinity and serve to improve the ductility of the coating where it is in contact with a roughening substrate or with the forming equipment.

Van Tijum worked also on the plasticity of the PET layer [17], [18]. This included the characterization of the polymer's response to a substrate with increasing roughness and the use of finite element simulations to explain how the roughening substrate profile affects the outer surface of the PET.

More recently, similar examinations have led to the development of predictive models [19]–[23] which describe polymers fairly well. This means in the case of PET taking into account a temperature-dependent aging component, amorphous and crystalline components and the resulting strain localization.

1.2.4 Metal plasticity

Electrochemically Chrome Coated Steel (ECCS) is a multi-layer system as well, as mentioned before. The ferritic phase and chromium phase have different modulus and hardness, but the same crystal structure (body centered cubic, space group $Im\bar{3}m$) and similar lattice parameter (Fe 0.287 nm, Cr 0.291 nm). Chromium oxide typically has a corundum structure (hexagonal, space group $R\bar{3}c$, a = 0.496 nm, c = 1.359 nm).

In the plastic response of metallic systems dislocations play a predominant role. Plastic deformation may result in the rotation of grains and in glide steps. Raabe et al. published [24] a nice overview of ten processes which may occur during metal deformation operating on various length scales from the single atom to the size of groups of grains. Each of these processes creates surface roughness in a different way and on a different length scale.

Wouters et al. researched the roughness evolution of aluminum surfaces [25] and other metals [26]. This roughness may be characterized by a statistical approach, with the surface described on a range of length scales by a fractal function. It was found that the correlation function used in this approach shows self-affine behavior up to a length scale called the correlation length, which in the case of textureless aluminum, iron and zinc was the grain size of the material. Related to that, they established that the roughness profile on the grain scale was strongly correlated with the sum of Schmid factors through the thickness of the material.

Soer et al. [27], [28] and Aifantis et al. [29] did impressive work on the mechanics of dislocations near grain boundaries. By means of nano-indentation, they investigated how the hardness of a material is affected by grain boundaries and how this fits into the well-known Hall-Petch theory. Additionally they illustrated yield excursions for indentations near these grain boundaries. They suggest that excess dislocations are pinned between the indenter and a type of barrier present at the interface. A sufficiently high stress removes the barrier, allowing the dislocations to move as a single burst.

The micromechanics of dislocations at heterogeneous interfaces are not fully established yet, but there is ongoing research on the matters of material properties near interfaces [30], nucleation of dislocations at heterogeneous interfaces [31], [32] and the inverse Hall-Petch effect [33]–[35]. The multi-scale nature of the behavior of heterogeneous metallic materials is extensively summarized by McDowell [36] from a modelling point of view, involving e.g. interface back stress and dislocation nucleation.

1.3 Objective

From the state-of-the-art it may be concluded that this thesis is not the first effort to understand the metal-polymer interface - and undoubtedly it is not the last. The aim of this project is to achieve an improved understanding of the microscopic processes which determine adhesion during and after forming, in order to be able to tailor the polymer-metal product with this knowledge.

Specifically, the changes in geometry and structure of the ECCS substrate are expected to play an important role by deforming the PET coating. The interplay between deformation of the ECCS, roughening of the interface on lateral scales equal to and smaller than the grain size, and de-adhesion of the PET from the substrate is to be studied in detail. The relevant processes are to be identified in the materials including their length scales. In addition, a number of experiments must be performed to quantify those processes and the relevant properties for each of the materials involved.

1.4 Characterization techniques

The research presented in this thesis was performed using a number of characterization techniques. Invaluable for the observation of surface topography and surface roughening are imaging techniques such as optical microscopy (OM) and scanning electron microscopy (SEM). On the other hand information about the composition or structure of materials typically requires techniques involving diffraction (e.g. electron backscatter diffraction, EBSD)

and/or the collection of spectra (energy-dispersive X-ray spectroscopy, EDX). In addition, sample preparation requires cross-sectioning ductile materials with very dissimilar hardness. Besides the standard metallographic polishing techniques, an important tool used to cross-section the two materials without introducing significant strain was the focused ion beam (FIB). The experimental equipment used in this research are shown in Table 1.1, and advantages of the three most important techniques are introduced in more detail in the paragraphs below.

Table 1.1: List of equipment

Equipment	Specification
Metallographic preparation	Struers grinding and polishing machines and consumables; Buehler Vibromet 2
SEM	Philips XL30 SEM FEG (Field Emission Gun) Philips XL30s SEM FEG Philips XL30 ESEM FEG
EBSD	TSL OIM system with digital camera
Dual beam (FIB and SEM)	Tescan Lyra\FIB-FEG
OM	Olympus VANOX-T
PIPS	Gatan PIPS (Precise Ion Polishing System)
DIC module	Aramis 5.3 software module
Calculation software	Wolfram Mathematica® 9.0
Tensile experiments	Kammrath and Weiss tensile/compression module
Sputter deposition	Technics Inc. Hummer

1.4.1 SEM

In a *scanning electron microscope* (SEM) electrons are emitted, accelerated and magnetically focused in a beam towards a sample in a vacuum chamber. These electrons interact with the surface material and their energy is dispersed, resulting in a variety of contrasting signals. This includes secondary and back-scattered electrons (SE, BSE), characteristic X-rays, cathodoluminescence, specimen current and transmitted electrons. Most of the research presented in this thesis was done using the so-called SE detector, although in certain cases the BSE detector adds valuable information by improving contrast between e.g. differently oriented metal grains.

The ability to analyze non-conducting samples using an electron-based technique like SEM is a mixed blessing. It is common to observe polymeric, rubber, glass or otherwise non-conducting samples after applying a nanometer thin conductive metal layer to the surface, and ensuring a well-conducting electrical contact of the resulting surface with the ground. However this additional layer interferes with surface sensitive measurements, and charge accumulation can still occur to a small degree. Furthermore, low electronic conductivity is often paired with low heat conductivity, and especially in the case of organic samples this might be cause of concern.

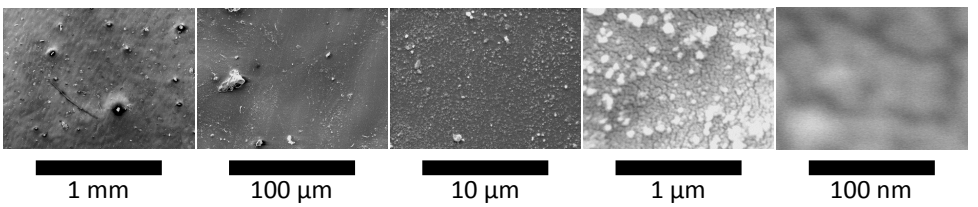

Figure 1.4: SEM images of strained PET/ECCS laminate. The PET surface is covered by a thin gold layer, deposited by sputter deposition. The conductivity is not as good as a metal sample's which limits the image quality; however the nanostructure of the gold layer can be distinguished in the rightmost images.

Still, the SEM has many valuable characteristics. It is unique in the flexibility of its focus and field of view; observations can be made at length scales spanning several orders of magnitude without changing hardware modules (see Figure 1.4). Since in this research the relevant length scale is not known *a priori*, flexibility in the observation is a critical issue. In addition the fine positioning of the electron beam is controlled by the column, so for a surface scan the sample simply remains stationary. This allows the introduction of custom sample holders and certain testing devices like the tensile module into the vacuum chamber, and makes in-situ measurement of properties with secondary devices possible.

The depth of focus of the electron beam is relatively large. It is possible to observe surfaces with a roughness exceeding 10 µm at a lateral length scale of 100 nm and even smaller. Furthermore the mechanical interaction of the measurement method with the sample is negligible and SEM observations are typically unaffected by mechanical properties like hardness.

In addition many parameters in the electron microscope can be adjusted to fit the needs of a sample. Acceleration voltage and current can be controlled, and scans of the surface can be made using a variety of patterns, pixel densities and collection times. Many SEMs include the possibility to tilt the sample, and there

is a variety of specialty microscopes available which fit additional needs such as the *environmental scanning electron microscope* (ESEM).

1.4.2 EBSD

One special SEM technique used extensively in the research described here (see chapter 6) is *electron backscatter diffraction* (EBSD), also known as *orientation imaging microscopy* (OIM). It is used for the characterization of crystalline materials such as metals and ceramics.

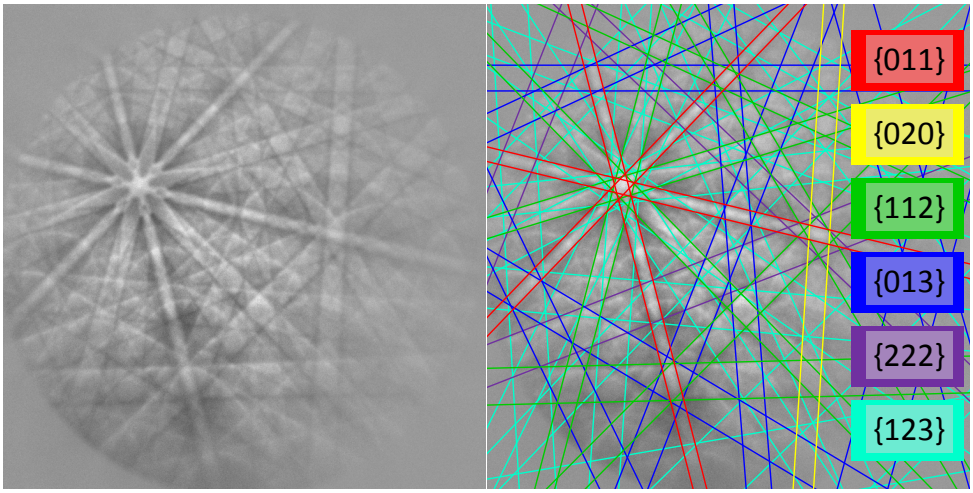

Figure 1.5: Kikuchi pattern produced by ferrite, a common body centered cubic (bcc) phase. The bands observed in the image originate from various reflectors, as illustrated on the right. $\{hkl\}$ *indicates all planes that are symmetrically equivalent to the* (hkl) *plane*

It operates on the principle that back-scattered electrons when leaving the sample surface undergo diffraction according to orientation and nature of the local crystal. The diameter of the interaction volume in which this diffraction occurs can be as small as 30 nm, so a diffraction pattern is generated from an extremely small volume. This diffraction pattern is commonly referred to as a Kikuchi pattern (see Figure 1.5) and it is collected on a cathodoluminescent screen which is filmed by a CCD camera.

It contains valuable information as to the space group and lattice parameters of the crystal, and knowing the relative position of the sample and the cathodoluminescent screen on which the pattern is collected the orientation of the crystal can be determined. Presently the technique has undergone significant development, and EBSD systems make full use of the resources available in a

scanning electron microscope. It is possible to automatically collect Kikuchi patterns from a large number of points on the surface, which results in a line scan or even a map of the surface with a high information density.

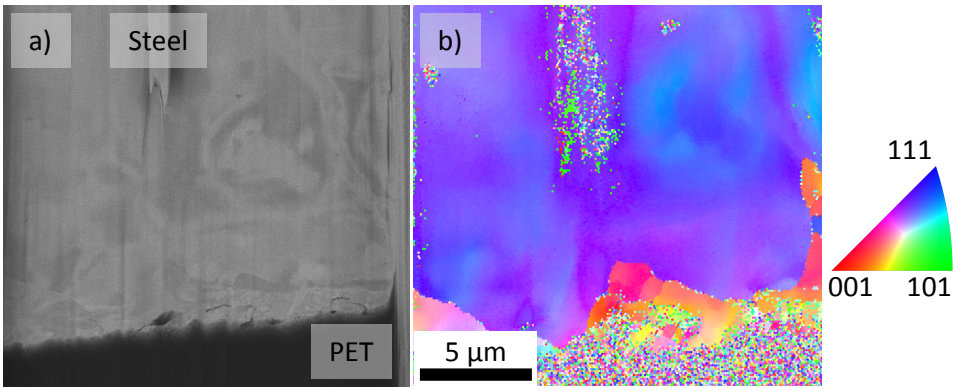

Figure 1.6: PET and ECCS cross-sectioned by FIB at glancing angle. (a) image of cross-section made with SEM (secondary electrons) and (b) IPF map of orientations at cross-section made by EBSD. The PET is amorphous and appears as noise.

Thus, the technique is used in practice in two ways. Firstly the information obtained from the pattern about the lattice, combined with other information (e.g. alloy composition) can be used to help identifying the phases present at a surface or cross-section; this may include making a map of the different phases, once the various phases are properly recognized. Secondly the technique is used for the quantification of texture and microstructure.

Texture in the classical sense originated from techniques like X-ray diffraction (XRD) which measure on a much larger scale, and thus typically collect orientation information of all grains in one measurement. Naturally the orientation information obtained by EBSD can be mixed together and analyzed in the same ways, given that the scanned area is representative of the bulk. But the microscopic nature of the technique, where each pixel is a separate measurement, also allows the researcher to obtain information about local features (e.g. how two grains are oriented relative to each other).

1.4.3 FIB

The *focused ion beam* is used as a precise machining tool rather than a measurement device, but in principle it is both. It is similar to an electron microscope in that a charged species is emitted, focused as a beam and accelerated towards a sample surface. However the charged species is an ion

rather than an electron – in this case gallium, although argon ions are commonly used as well.

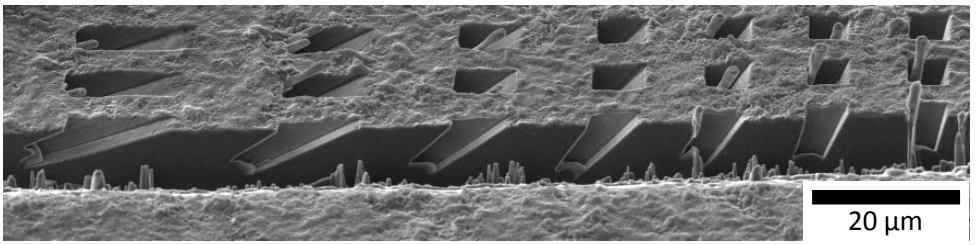

Figure 1.7: PET surface observed with SEM under a 55° angle, with holes etched in the surface by FIB. Different volumes of material have been etched due to variation in angle of incidence.

Because the Ga^+ species has a five orders of magnitude higher mass than the e^- in an SEM, it has a much larger momentum at the same acceleration energy, and a very different interaction with the sample surface. Given a well-focused ion beam images can be generated from the secondary electrons generated in the collisions with the surface. The penetration depth is much less than in the case of electrons and so the obtained image is different; more sensitive to the topography of the surface. Impingent ions collide with atoms in the sample and displace them. This can be used to eject material from the sample into the vacuum chamber. With control of the beam position and dwell time, custom shapes can be etched.

The ion beam we used is part of an SEM/FIB dual beam system, in which the SEM can be employed for imaging and positioning of the sample and for local deposition of material (e.g. silicon oxide) by electron-induced dissociation of precursors. The FIB part can be used to image the sample at a low current or etch the sample at a high current. In principle observations can also be done at a high ion current and even the lowest current etches the sample; the difference in current results only in a dissimilar minimum spot size and etch rate. The ion beam column is oriented at 55° to the electron beam column, and the sample stage can tilt, rotate and move so that the sample can be irradiated from almost any direction.

The focused ion beam is routinely used to produce samples for small-scale observations such as transmission electron microscopy, and specific procedures are followed to limit the effects of heating, ion implantation and surface amorphization. In addition, surfaces prepared by FIB can be used in crystallographic analysis like EBSD, although the serial nature of the etching

technique rather limits the amount of surface which can reasonably be prepared by FIB.

The rate of etching is a function of the incident current, the acceleration voltage (typically 30 kV), the sample structure and chemical composition, and finally the sample geometry and effective incident angle. Most of these parameters once optimized are fixed, so the required time increases in a linear manner with the etched volume.

1.5 Outline of the thesis

The contents of this thesis can be grouped in two subjects. Firstly, a novel characterization technique has been developed. This method is explained in chapter 2 and tested in chapter 3. In chapters 4 and after the scientific progress on characterizing the studied metal-polymer interface is discussed. While chapter 2 and 3 should be read together, the other chapters may be read separately. It is therefore possible that some of the information used in a particular chapter is repeated in the respective introduction.

In chapter 2 the novel method is explained and illustrated by which images obtained in an SEM may be used to characterize the topography of a surface in 3D. The sample is tilted between images, so the sample is imaged in several different orientations – this is essentially a form of stereoscopy. While similar methods can be found in the literature, this method has several unique characteristics and advantages. Most importantly, information about the SEM setup, the orientation of the sample and the amount or direction of the tilting is not required. Instead the relevant parameters are calculated from the images. Using this method, the geometries of sample surfaces are calculated in three dimensions.

In chapter 3 several experiments are presented to illustrate the limits and uses of this 3D geometry characterization method. Firstly, the method is tested using data generated by a computer rather than measured on a sample. This verifies that the method is working in the ideal case as well as after the introduction of well-quantified amounts of random Gaussian noise. Secondly the most common issue encountered in SEM, image distortion due to electric charge accumulation, is investigated. Thirdly the method is applied to a sample of ECCS which is strained in tension. It is demonstrated how the surface topography can be used to obtain displacement data in three dimensions.

In chapter 4 the question of ECCS-PET adhesion loss and pitting corrosion resulting from DRD deformation is investigated. The laminate material is cross-sectioned by FIB and small pockets are demonstrated at the metal-polymer interface – here the adhesion is lost i.e. the interface is delaminated locally. Furthermore the geometry of this interface is investigated from the cross-sections, and small overhanging shapes are found. It is argued that these overhanging shapes, formed by the compressive strain in the DRD process, play a crucial role in the delamination process.

A prevalent assumption and/or hypothesis at this time was that the evolving roughness exerts work on the PET, and that after a critical amount of work is stored in the PET the interface would delaminate. Searching for confirmation of this cracking mechanism, expressions of work of adhesion were formulated based on the interface curvature (due to the overhanging geometric features). The problem was studied keeping in mind the unknowns such as length scale and dissipation volume. However after failing to find any correlation between the locations predicted by such a calculation and the actual locations of pockets found at the interface, we concluded that this critical work hypothesis was inaccurate. Subsequently, our attention turned to a different type of experiment.

In chapter 5 a cross-sectioned PET-ECCS laminate sample is strained in tension in situ. A crucial observation here is that the glide steps originating from deforming surface grains cause strain localization in the PET. This causes the etched PET to form crazes perpendicular to the applied stress, including the formation of fibrils. This behavior is not typical of the PET used; crazes would be expected at a much larger strain. So, the effects of focused ion beam etching on the mechanical properties of PET are explored. It is found that ion etching changes the mechanical properties of the affected PET, reducing the toughness. This may be explained by scission caused by the impingent ions, which serves to reduce polymer chain length before the polymer can be etched. The same crazes are not formed if the PET is ion etched after it has been strained.

In chapter 6 the roughening along the ECCS-PET interface is studied in relation to the microstructure of the underlying steel. This microstructure is measured in terms of orientations by EBSD, and is presented in several ways in order to determine how the roughening behavior depends on the steel microstructure. The relative plasticity of the steel grains is shown as Taylor factors, and the curvature of the steel lattice is calculated. This allows the observation of sub-grain boundaries which appear to be present specifically in the more compliant grains; however the lattice curvature has no correlation with the interface

curvature. It is concluded that roughening of the interface on the sub-grain scale is the result of dislocation slip.

The thesis completes with a summary and outlook in chapter 7.